

Investigation of Pre-Purification unit in cryogenic air separation process

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Abstract

Cryogenic air separation processes are routinely used in medium to large-scale plants to produce nitrogen, oxygen, and argon as gases and/ or liquid products. Cryogenic air separation is the preferred technology for producing very high-purity oxygen and nitrogen. Various processes are needed in a cryogenic air separation plant, of which the fundamental ones are: air compression, air purification, heat exchanging, distillation and product. One of the most important parts of the ASU process is air purification. Because the exchangers can be frozen by Carbon and water. Factors that cause the inactivation of absorbents include sticking together, mechanical factors, absorption of unwanted substances, failure to desorption of absorbed substances, wetting of the cavity inlet opening due to incompatibility or maloperation and temperature factors. In this study, a pre-purifier unit in the cryogenic air separation process is investigated.

Keywords: Cryogenic, Oxygen, pre-purification, Absorber, Cold box

1. INTRODUCTION

The use of oxygen in medical purposes and foundry industries, welding, refinery units, petrochemical, steel, and cooling processes increased the importance of the production of this material in the last few decades. Three methods for air separation are commercially available: cryogenic distillation, pressure swing adsorption, and membrane separation. The cryogenic method is based on the liquefaction of air. The method of adsorption which air passes through a bed filled with an absorbent, and oxygen-rich flow is produced based on selective absorption [1]. The membrane separation method is based on the relative permeability of the components in the air. Due to the pressure difference between the two sides of the membrane, oxygen from the air separated [2]. Although other technologies are investigated, cryogenic air separation technology is the most common and standard technology for producing oxygen products in liquid form. The cryogenic method is mostly used to produce with high amounts and purity, mostly. Cryogenic distillation is normally adopted for air separation in steelworks and methanol factories due to the demanding oxygen purity requirement (>99.5 mol%). This method is one of the most expensive and efficient methods of high production of oxygen, nitrogen and argon gas in the industry. Air separation units use several distillation columns to produce liquid gases with high purity from compressed air. In this technology, pure nitrogen is produced as a by-product. Research shows that cryogenic oxygen production has increased in recent years. The type of process can be different based on the amount of purity and product flow rate. The properties of various cryogenic processes for air separation depend on the amount of pressure at the inlet or outlet of the products [1,3].

Although cryogenic distillation can separate high-purity oxygen from air, it is well known that cryogenic distillation requires a large amount of energy to liquefy air by cooling [2,4]. To produce liquid nitrogen during cryogenic distillation, a two-column separation process, consisting of low and high-pressure columns, has been developed and is widely used. By combining the condenser of the high-pressure column with the reboiler of the low-pressure column, the latent heat of the vaporization of air can be exchanged with the

condensation heat of pure nitrogen in the two-column separation process [1,3,4,5]. Thus, not only is nitrogen liquefied in the process but also the energy consumption of the process can be decreased by heat exchange. However, a large pressure difference is required between the high and low-pressure columns for the exchange of vaporization heat with condensation heat. Therefore, the energy cost for producing pure oxygen still remains quite high due to the work needed to compress the air feed [6].

2. SEPARATION METHODS

Three separation methods are predominant for separating constituent gases from the air [3].

- Membrane separation
- Pressure swing adsorption
- Cryogenic distillation process

2.1. MEMBRANE SEPARATION

In this separation process, equipment pumps air into the membrane module and the targeted gases like oxygen and nitrogen are separated based on differences in diffusivity and solubility. For example, oxygen can be separated from the ambient air and collected at the upstream side, and nitrogen at the downstream side [5].

2.2. PRESSURE SWING ADSORPTION

The principle of Pressure Swing adsorption (PSA) is the amount of adsorbate deposited on the adsorbent increases with increasing pressure. Adsorption increases with increasing pressure and desorption occurs at low pressure. The technique is applied for the adsorptive recovery of O₂ and N₂ from the air [6].

2.3. CRYOGENIC DISTILLATION PROCESS

Cryogenic separation is a commercial process that takes place at very low temperature, where the component of feed gas starts to liquefy [76–81]. An additional compression and cooling for the feed gas is necessary for process operation. The cryogenic method has been explained at follows [7].

3. COMPARISON OF SEPARATION METHODS

The three separation techniques have different process properties, and there is a requirement for different ranges of investment and operating costs. Table.1. characterizes these segments by their production capacity and gas purity. Of course, the numbers given in the table therein are no sharp limits but indicate reasonable application ranges [8].

Table.1. Comparison of separation methods [4,5,7]

Gas	Capacity (Mn ³ h ⁻¹)	Typical purities	Preferred Separation Method	Load Range
N ₂	1-1000	<99.5% (including argon)	Membrane	30-100%
N ₂	5-5000	<99.99% (including argon)	Pressure Swing Adsorption	30-100%
N ₂	200-400000	Any with residual concentrations down to the ppb range	Cryogenic rectification	60-100%
O ₂	100-5000	<95%	Vacuum Pressure Swing Adsorption	30-100%
O ₂	1000-150000	Any with residual concentrations down to the ppb range. (O ₂ content mostly>95%)	Cryogenic rectification	60-100%
Ar	-	-	Cryogenic rectification	-

The operating costs of the separation processes are mainly determined by their energy consumption. Tables 2 and 3 show the specific energy demand for the production of N_2 and O_2 by the three separation methods. The figures are only guidelines. However, the actual values depend on the detailed process design. Cryogenic air separation requires the smallest work, which, however, is still significantly larger than the minimal separation work needed for a completely reversible process.

Table 2. Comparison of separation methods at O_2 content in nitrogen [6,7]

O_2 content in nitrogen	2%	0.5%	0.1%	1 ppm
Membrane	0.43	0.65		
Pressure Swing adsorption	0.26	0.34	0.45	
Cryogenic rectification				0.15-0.25
Theoretical minimal separation work				0.08

Table 3. Comparison of separation methods at O_2 Purity [6,7,8]

O_2 Purity	90%	93%	99.5%
Pressure Swing adsorption	0.36	0.39	0.45
Cryogenic rectification		0.32	0.35
Theoretical minimal separation work			0.07

3.1. PROCESS DESCRIPTION OF CRYOGENIC SEPARATION PROCESS

The cryogenic separation process requires a very tight integration of heat exchangers and separation columns to obtain a good efficiency and all the energy for refrigeration is provided by the compression of the air at the inlet of the unit. Processes involved in cryogenic air separation is shown in Figure 1.

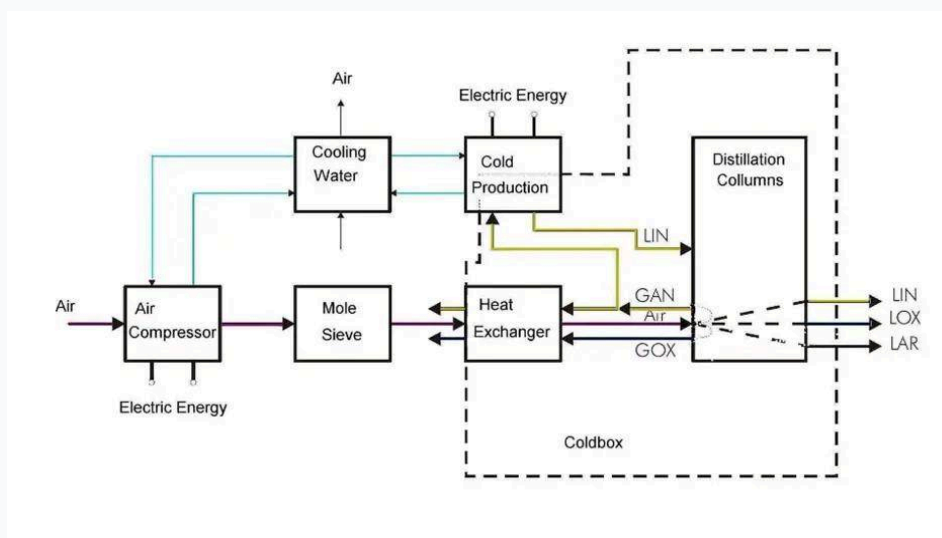


Figure 1. Processes involved in cryogenic air separation [2]

To achieve low distillation temperatures, an air separation unit requires a refrigeration cycle that operates by means of the Joule–Thomson effect, and the cold equipment has to be kept within an insulated enclosure (commonly called a "cold box"). The cooling of the gases requires a large amount of energy to make this refrigeration cycle work and is delivered by an air compressor. Modern ASUs use expansion turbines for cooling; the output of the expander helps drive the air compressor, for improved efficiency. The process consists of the following main steps[⁹]: Before compression the air is pre-filtered of dust [9].

Air is compressed where the final delivery pressure is determined by recoveries and the fluid state (gas or liquid) of the products. Typical pressures range between 5 and 10 bar gauge. The air stream may also be compressed to different pressures to enhance the efficiency of the ASU. During compression, water is condensed out in inter-stage coolers. The process air is generally passed through a molecular sieve bed, which removes any remaining water vapour, as well as carbon dioxide, which would freeze and plug the cryogenic equipment. Molecular sieves are often designed to remove any gaseous hydrocarbons from the air since these can be a problem in the subsequent air distillation that could lead to explosions.[8] The molecular sieve bed must be regenerated. This is done by installing multiple units operating in alternating mode and using the dry co-produced waste gas to desorb the water. Process air is passed through an integrated heat exchanger (usually a plate-fin heat exchanger) and cooled against product (and waste) cryogenic streams. Part of the air liquefies to form a liquid that is enriched in oxygen. The remaining gas is richer in nitrogen and is distilled to almost pure nitrogen (typically < 1ppm) in a high-pressure (HP) distillation column. The condenser of this column requires refrigeration which is obtained from expanding the more oxygen-rich stream further across a valve or through an expander (a reverse compressor). Alternatively, the condenser may be cooled by interchanging heat with a reboiler in a low-pressure (LP) distillation column (operating at 1.2-1.3 bar abs.) when the ASU is producing pure oxygen. To minimize the compression cost the combined condenser/reboiler of the HP/LP columns must operate with a temperature difference of only 1-2 K, requiring plate fin brazed aluminum heat exchangers. Typical oxygen purities range from 97.5% to 99.5% and influence the maximum recovery of oxygen. The refrigeration required for producing liquid products is obtained using the Joule–Thomson effect in an expander which feeds compressed air directly to the low-pressure column. Hence, a certain part of the air is not to be separated and must leave the low-pressure column as a waste stream from its upper section. Figure 2. show the vapour pressure curves of atmospheric gases [1,5,10].

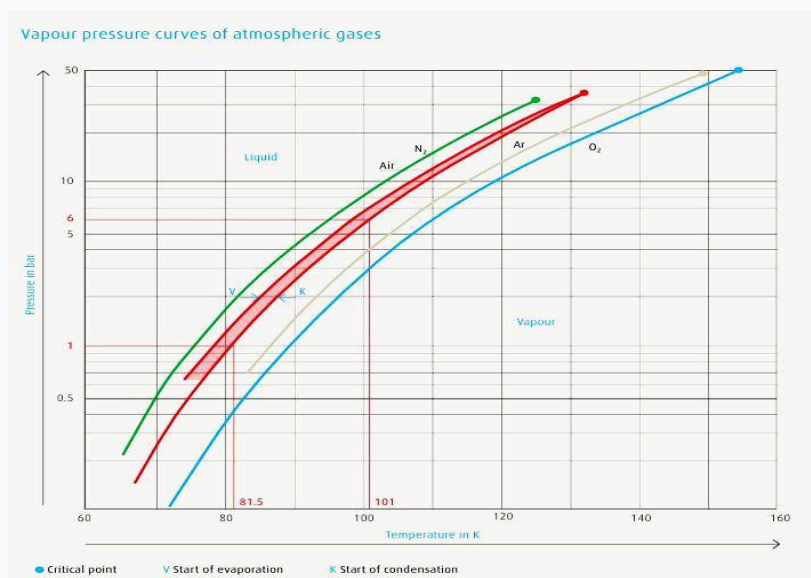


Figure 2.vapour pressure curves of atmospheric gases [6]

4. PRE-PURIFICATION UNIT

One of the most important parts of the ASU process is the heat exchangers in order to reduce the temperature of the compressed air. One of the most important process challenges in these exchangers that reduces their performance can be caused by Carbon and water freezing. In this context, adsorbents can be Efficient and effective in some way and remove water and carbon dioxide. The Pre-purification system is designed to remove water vapour, carbon dioxide, and other potentially unsafe impurities contained in the incoming process air. This is important for the safe operation of the plant as it ensures that the water and carbon dioxide do not enter the cryogenic portion of the plant where they could plug the main vaporizer exchange passages placed in the cryogenic distillation column. Plugged passages can lead to 'dead-end boiling' of liquid oxygen creating areas of localized high concentrations of impurities (e.g.; hydrocarbons) within the main vaporizer [3]. The Pre-purification system effectively stops ozone, acetylene, and propylene. It also partially adsorbs propane and ethylene. All of these components are hazardous if found in the cryogenic portion of the plant and will eventually accumulate in the liquid oxygen main vaporizer bath and increase the process risk of explosion in some plants. Pre purification system (PPU) is also known as the Air purification system (APU) and Front End Purification system (FEP) [4]. The chilled air stream is fed to a dual-bed pre-purification system. The pre-purifier bed design utilizes, as an adsorbent, a layer of molecular sieves and a layer of activated alumina. An absorbent layer of active alumina is used to remove the initial humidity of the inlet air to PPU and a molecular sieve layer is used to remove carbon dioxide and complete dehumidification. As the process air stream is fed to one bed, all remaining water vapour, carbon dioxide, heavy hydrocarbons and some lighter hydrocarbons are removed, while the second bed is simultaneously regenerated with waste nitrogen gas previously heated in a regeneration heater. The beds are switched at a predetermined cycle time. After passing through a dust filter, a small amount of clean dry air from the prepurifier system is drawn off for plant instrument air and a certain amount is sent to the customer as instrument and plant air [10].

Activated alumina and molecular sieve are used for adsorb water as adsorbents. Activated alumina and molecular sieves have a strong adsorption capacity for water vapour. Activated alumina (alumina adsorbent) is also integrated with a lot of good physical and chemical properties such as high strength, not powder, so in most cases is the first choice for an adsorption dryer. In particular, in the absence of thermal regeneration, activated alumina (alumina adsorbent) is almost inevitable to obtain compressed air at -40°C dew point [5,8]. However, the adsorption capacity of activated alumina (alumina adsorbent) is much less than molecular sieve in the low-water environment, so if you want to get highly dry compressed air (pressure dew point below -60 °C), the molecular sieve is very useful. However the mechanical strength and anti-water droplet performance of molecular sieves are not ideal, it is often combined with a certain percentage of alumina used to obtain the best results [5,7]. Recycling activated alumina (alumina adsorbent) is low price. The product appearance is also white, which makes it difficult to distinguish good and bad, but after the use of six months, bad activated alumina will be powdered, and the device and result in losses. So customers who choose products must be careful, to choose good companies [7]. How to choose the right desiccant, for the customer's needs according to their specific equipment, such as gas pressure, and the amount of processing to choose the right product.

Figure 3. show the alumina and molecular sieve applied in the Polypropylene Sepehr Mokran company air separation unit.



Figure 3. alumina and molecular sieve

The strength of active alumina is higher than molecular sieve, but it should be noted that due to more water tendency to absorb, the erosion rate of active alumina is higher. The level of the adsorbents inside the vessels should be kept high and the level checked by the operator semiannually. In these vessels, humid air enters from the bottom and sides and exits from the center and top of the tower. It will cause the efficiency of the upper part of the vessels to be lost if the level of the adsorbents is reduced and the absorption process will not be performed well. These vessels should be charged every six months [9].

Adsorption is done at high pressure and low temperature, and regeneration is achieved at the reverse of absorption (low pressure and high temperature).

The regeneration process is carried out in 7 steps:

- 1) Depressurizing 2) Heating 3) Cooling 4) Pressurizing 5) Parallel 6) Change

In order to prevent absorber damage, pressurizing and depressurizing should be done slowly because the beds are sensitive to pressure changes.

Factors that cause the inactivation of adsorbents [4,5,6,7]:

- 1) Sticking together 2) Mechanical factors 3) Absorption of unwanted substances 4) Failure to desorption of absorbed substances 5) Wetting of the cavity inlet opening due to incompatibility or maloperation 6)

Temperature factor

Sintering or clumping is an undesirable and common phenomenon in absorption towers. This phenomenon is dependent on temperature and thermal shocks. Sintering is shown in the Figure 4.

This phenomenon is caused by an increase in temperature. The adsorbent activity is reduced and it should be changed over time. Failure to desorption of absorbed materials causes adsorbent poisoning and decreasing in the active surface. Adsorption is based on the empty surface. When the Porous surfaces are filled, the amount of adsorption decreases and the absorber becomes inactive.



Figure 4. Sintering of absorber

If the level or efficiency of the absorbers decreases, some moist air exits without absorbing impurities and the amount of water and CO₂ it into the cold box. These impurities caused clogging of the fin-plate exchanger in the cold box and cryogenic pump inlet strainers. The bed absorbs more CO₂ gradually and a large part of the bed is saturated. This area should not reach the air outlet. In this situation, CO₂ absorption is not accrued completely. There is a temperature drop due to the desorption of CO₂ and water at the beginning of heating since evaporation is an endothermic process. During desorption, CO₂ is separated at first and then water. Figure 5. shows the temperature peak of regeneration and the diagram of regeneration gas.

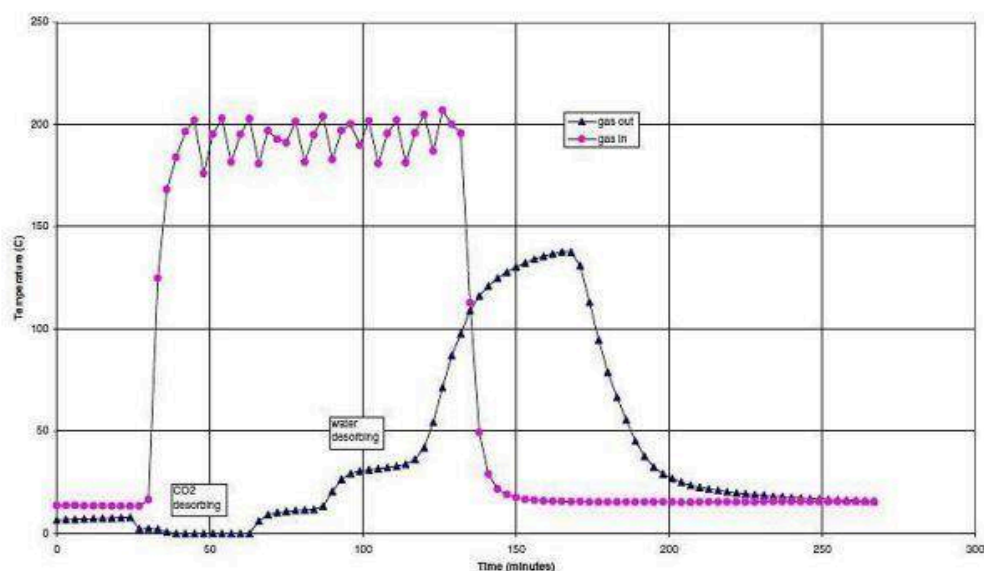


Figure 5. the temperature peak of regeneration and the diagram of regeneration gas

According to the curve, the temperature of the regeneration gas at the outlet of the bed has not change significantly at the beginning of the heating step. In this case, all the heating heat is used to remove CO₂ and water. After that, the temperature increases to 40 °C. This situation remains at the mentioned temperature at the specified time. The maximum volume of water is desorbed and exited in the absorber. This area is called

Plateau. After this step, the temperature is increased again until it reaches the maximum value (130 °C). The incremental changes in temperature up to 130 indicate that no impurities in the system.

5. CONCLUSION

The cryogenic air separation process is today's preferred route for the supply of industrial gases to large facilities. PPU is the key process in cryogenic air separation and has consequently been given special consideration in this study. The process air is generally passed through a molecular sieve bed, which removes any remaining water vapour, as well as carbon dioxide, which would freeze and plug the cryogenic equipment. Molecular sieves are often designed to remove any gaseous hydrocarbons from the air since these can be a problem in the subsequent air distillation that could lead to explosions. The molecular sieve bed must be regenerated. This is done by installing multiple units operating in alternating mode and using the dry co-produced waste gas to desorb the water. The sticking together, mechanical factors, absorption of unwanted substances, failure to desorption of absorbed substances, wetting of the cavity inlet opening and sintering cause damage to the adsorbent and reduce the efficiency of pre-purification.

6. ACKNOWLEDGEMENTS

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7. NOMENCLATURE

ASU	air separation unit
PPU	pre-purifier unit
APU	air purification system
FEP	Front End Purification system
LP	low pressure
HP	High pressure

8. REFERENCES

References, as the final part of each paper, should be written by Times New Roman 10 pt. They are to be numbered in the order they appear in the main text and referenced just by numbers within brackets, e.g. [3]. Only references, which are cited in the paper, should be included. For each reference, adequate specifications should be mentioned according to a standard format such as the following examples. If you are indicating a document published in the Persian language please add the expression '(in Persian)' at the end of it.

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